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## (54) METAL-MODIFIED APATITE AND ITS PRODUCTION

### (57)Abstract:

PROBLEM TO BE SOLVED: To keep excellent adsorption characteristics developing new catalytic function over a long period by forming a metal oxide having photo-catalytic action in an apatite crystal structure by coprecipitation to cause ion exchange treatment.

SOLUTION: A metal-modified apatite is produced by coprecipitating an apatite and a metal oxide having photo-catalytic action to composite the above components in atomic order and subjecting a part of the metal ion in the apatite crystal to ion-exchange with the metal ion of the metal oxide. The apatite is e.g. hydroxyapatite, fluoroapatite, etc., preferably calcium hydroxyapatite and the metal oxide is e.g. zirconium oxide, iron oxide, tungsten oxide, etc., preferably titanium oxide (TiO<sub>2</sub>). The content of the metal ion in the apatite crystal is at most about 15 mol%, preferably about 3-11 mol%.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] in addition to the biocompatibility and the adsorption property that an apatite does so, a photocatalyst function can be discovered if this invention is described in more detail about an apatite -- especially in the field of electronics, it is related with the useful apatite by which metal qualification was carried out. This invention relates to the manufacture approach of such a metal qualification apatite again.

[0002]

[Description of the Prior Art] It is known that semi-conducting material, such as titanium oxide, will do a photocatalyst function so. That is, in such semi-conducting material, if it absorbs the light energy of the wavelength equivalent to the band gap of a valence band and a conduction band, the electron of a valence band will move to a conduction band by excitation, and an electron hole will occur in a valence band. In a conduction band, the electron which has moved to it moves to the organic substance on the front face of semi-conducting material, and it is returned, and the electron hole generated there takes an electron in a valence band, and the organic substance is oxidized noting that a certain matter (for example, organic substance) is made to adsorb on the surface of semi-conducting material. Especially in titanium oxide, since the electron hole of a valence band has very strong oxidizing power, there is capacity which disassembles the organic substance into water and a carbon dioxide eventually. Using the titanium oxide film as an antimicrobial agent, a germicide, a deodorant, an environmental depurator, etc. is performed using the photocatalyst function (oxidization disassembler) of such titanium oxide. However, since titanium oxide itself does not have the property of adsorbing a certain matter on the front face, there is a limitation in the oxidative degradation function obtained.

[0003] On the other hand, it is calcium hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6 \cdot 2\text{H}_2\text{O}$  (it is hereafter described also as CaHAP) is the principal component of living body hard tissue like a gear tooth or a bone, and has a cation, a various anion and a various ion-exchange provoking therefore high biocompatibility, and an adsorption property. Calcium hydroxyapatite follows and research has been briskly done about the application to broad fields, such as adsorbents for chromatographies including biomedical materials, such as a dental implant, an artificial bone, and an artificial organ, a chemical sensor, an ion exchanger, and a catalyst. Especially calcium hydroxyapatite has the capacity to adsorb the organic substance, such as protein, specifically.

[0004] Recently, although it is not what meant application in the field of electronics especially paying attention to the electrical characteristics of semi-conducting material, such as titanium oxide, the development and research of a product which can pull out both property effectively are done combining semi-conducting material, such as two kinds of matter which was described above, i.e., titanium oxide etc., and calcium phosphate system compounds, such as CaHAP.

[0005] For example, the antimicrobial agent characterized by carrying out coat inclusion of one or more sorts of metallic compounds of Ti, Zr, or Zn on the front face of the poorly soluble phosphate (preferably hydroxyapatite) which supported complex ion at least as antibacterial ion is indicated by

JP,6-172113,A. Moreover, the filter characterized by having distributed and included amorphous calcium phosphate (tricalcium phosphate which contains water of crystallization preferably), and optical semi-conductor constituents (preferably titanium oxide, a cadmium sulfide, etc.) in the base material (preferably paper, textile fabrics, a nonwoven fabric, or plastic foam) fabricated in the shape of a sheet, or amorphous calcium phosphate and an optical semi-conductor constituent having pasted such a base material through adhesives is indicated by JP,10-33921,A.

[0006] Recently, it sets to JP,10-244166,A more. Activated carbon, Base materials, such as an activated alumina, silica gel, glass, form ceramics, and foam plastics, are prepared. The base material which forms in the front face of the base material the film which consists of titanium oxide, or consists of a titanium oxide particle is prepared. It is porosity calcium phosphate (preferably) to the front face of the titanium oxide film or a titanium oxide particle. The environmental clarification ingredient characterized by carrying out the coat of hydroxyapatite, the fluoridation apatite, etc. and the ingredient for specifically performing sterilization of clearance of an offensive odor, the harmful matter in air or decomposition clearance of dirt, waste water treatment, and water etc. are indicated. Such an environmental clarification ingredient can be formed by immersing a base material or a titanium oxide particle with the titanium oxide film into the false body fluid which adjusted a presentation, pH, etc. so that it might be easy to generate the film of porosity calcium phosphate. However, such a photocatalyst function high enough cannot be made to discover that in the case of this environmental clarification ingredient it may be satisfied in the titanium oxide used as a substrate although that coating is porosity how, since it has the structure which carried out the coat of the film of titanium oxide, or the front face of a particle with calcium phosphate. That is, since sufficient quantity of light does not reach titanium oxide, there is titanium oxide to inactive raw one and it has a possibility of causing decline in oxidative degradation effectiveness on the contrary. Moreover, since possibility of having stopped at the front face of the coating is high, without the organic substance which stuck to calcium phosphate coating on titanium oxide moving from the strength of the adsorption power which the coating has to the place of titanium oxide, oxidative degradation by the photocatalyst is not worn. If it becomes so, since any will reach an adsorption equilibrium, the adsorption power over the organic substance of calcium phosphate coating etc. will decline remarkably.

[0007]

[Problem(s) to be Solved by the Invention] The object of this invention can develop further the catalyst function in which various kinds of apatites including calcium hydroxyapatite do so, in view of the actual condition of a Prior art which was described above, and can make a new catalyst function discover. And it is in the thing which can maintain the outstanding adsorption property over specific sorbates, such as the organic substance, originating in an apatite over a long period of time simultaneously and for which the useful apatite by which metal qualification was carried out is offered especially in the field of electronics.

[0008] Another object of this invention is to offer the approach that the outstanding apatite by this invention by which metal qualification was carried out can be manufactured with simple and high dependability.

[0009]

[Means for Solving the Problem] this invention persons by compound-izing apatites including calcium hydroxyapatite, and the metallic oxide which has a photocatalyst operation by different technique from a Prior art lately Namely, the metal ion of the metallic oxide which has a photocatalyst operation for some metal ions under apatite crystal (for example, the case of calcium hydroxyapatite calcium ion) (-- for example, it discovered that a technical problem which was described above can be solved with the compound-ized technique in the atomic level which consists of carrying out the ion exchange to titanium ion) in the case of titanium oxide.

[0010] This invention is in the metal qualification apatite characterized by forming the metallic oxide which is formed by the coprecipitation method and has a photocatalyst operation of the ion exchange into the apatite crystal structure in the one field. In the field of another, this invention is for manufacturing the metal qualification apatite of this invention, and is in the manufacture approach of the

metal qualification apatite characterized by adding to the configuration ion of an apatite beforehand and preparing the metal ion of the specified quantity of a metallic oxide with a coprecipitation method under both coexistence.

[0011]

[Embodiment of the Invention] When the metal qualification apatite by this invention and its manufacture approach are explained about the gestalt of the desirable operation, they are as follows. In addition, please understand that this invention is not what is limited to the gestalt of the following operation. In the apatite by this invention by which metal qualification was carried out, the following general formulas can express fundamentally the apatite which constitutes the subject.

[0012] In  $Ax z X (BOy)$  top type, A expresses various kinds of metal atoms, such as calcium, Co, nickel, Cu, aluminum, La, Cr, Fe, and Mg, and B expresses atoms, such as P and S, and X is a hydroxyl group (-OH), a halogen atom (for example, F, Cl), etc. Although not necessarily limited to what is enumerated below as an example of such an apatite, they are an apatite, hydroxyapatite, a fluoro apatite, a chloro apatite, tricalcium phosphate, calcium hydrogen phosphate, etc. the calcium hydroxyapatite whose A the apatite which can be suitably used in operation of this invention is hydroxyapatite whose X in a top type is a hydroxyl group, and X in a top type is a hydroxyl group still more preferably, and is calcium (calcium) (CaHAP), calcium<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub> [i.e., ], 2 it is. Therefore, explanation of the apatite of the following this inventions is given to explain especially with reference to CaHAP.

[0013] In the metal qualification apatite of this invention, having carried out the ion exchange of some metal ions under apatite crystal to the metal ion of the metallic oxide which has a photocatalyst operation considers as the description by compound-izing an apatite and the metallic oxide which has a photocatalyst operation on atomic level with a coprecipitation method. As this shows typically drawing 1, the apatite field 3 which is adsorption site [ of specific sorbates (not shown), such as the organic substance, ] a, and the metallic-oxide field 4 which is the sorbate decomposition site b depending on a photocatalyst operation can be intermingled on the scale of atomic level on the same crystal face, therefore adsorption and decomposition of a sorbate are performed efficiently simultaneous to homogeneity. Moreover, the ion-exchange method based on the coprecipitation method adopted by this invention In production of the titanium oxide film by the sol-gel method adopted with the conventional technique referred to previously In order to make with the crystal structure of the titanium oxide in which photocatalyst activity is shown, in spite of not forming the crystal structure of the metallic oxide in which being heat-treated in about 500-degree C high temperature has unnecessary heat treatment by contrast, and photocatalyst activity is shown The outstanding photocatalyst activity can be embodied.

[0014] Although the example of the highly efficient composite material 10 which formed the metal qualification apatite 2 with the thin film on the base material 1 is shown by drawing 1, the gestalt of operation of this invention is not limited only to this. That is, although explained below, the metal qualification apatite of this invention may be removed, after using it temporarily and completing those production, only when it is not necessary to have the base material or and the thin film of a metal qualification apatite, a film, a sheet, etc. are produced.

[0015] Moreover, in the metal qualification apatite of this invention, especially the thing for which an apatite field and a metallic-oxide field are intermingled on the scale of atomic level on the same crystal face could be easily understood from drawing 2 which shows the surface structure model of Ti ion-exchange CaHAP. Although various kinds of metallic oxides with which usefulness is known in this technical field as a metallic oxide which has a photocatalyst operation can be used when carrying out the ion exchange of some metal ions under apatite crystal to the metal ion of the metallic oxide which has a photocatalyst operation according to this invention Preferably, the oxide of metals, such as titanium, a zirconium, iron, and a tungsten, can be used, and it is the oxide 2 of titanium, i.e., TiO, still more preferably. It can be used. Therefore, it especially sets to the following explanation and is TiO<sub>2</sub>. This invention is explained with reference to an activity.

[0016] When performing the ion exchange using a metallic oxide according to this invention persons' knowledge, the content of the metal ion of the metallic oxide is a ratio with the metal ion under apatite crystal, is 15-mol [ a maximum of ] %, and although it is widely said according to the result considered

as a request that it can change, even if it exceeds 15-mol %, it cannot usually expect more remarkable effectiveness. generally the 3-11-mol range of the content of a metal ion is % in metal ion ratios, such as calcium ion, -- desirable -- ten-mol % -- it is most desirable that it is less than [ order or it ].

[0017] The metal qualification apatite of this invention can be offered with various configurations and dimensions according to the factor of the purpose for spending, and manufacture conditions and others. As a suitable configuration, a particle, a tablet, a rod, a plate, a block, a sheet, a film, a thin film, etc. can be mentioned, for example. Moreover, since in the case of a sheet, a film, a thin film, etc. those ingredients may be used independently, otherwise this apatite constitutes a highly efficient composite-construction object, it may be used combining a base material in the form covered especially to one side or both sides of a base material. as a base material used here, it is not necessarily limited to what is enumerated below -- also although kicked, the foil of various kinds of ingredients, such as paper (a synthetic paper etc. is included), textile fabrics or a nonwoven fabric, timber, glass, a metal, ceramics, and plastics, a film, a sheet, a plate, etc. can mention others. These base materials may be porosity if needed. Especially the metal qualification apatite of this invention can be advantageously used in the form formed as a thin film on the surface of the base material.

[0018] Advantageously, the metal qualification apatite of this invention characterized by forming a metallic oxide which was explained above into the apatite crystal structure adds beforehand, the metal ion, i.e., the start raw material, of the specified quantity of a metallic oxide, the configuration ion, i.e., the start raw material, of an apatite, and can compound it with a coprecipitation method under both coexistence.

[0019] He could understand easily especially the manufacture approach of the metal qualification apatite by this this invention from drawing 3 which shows a part for the first portion of the production process of Ti ion-exchange CaHAP. That is, to the pure water which carried out :decarbonation processing, the start raw material of titanium oxide, i.e., the solution of sulfuric-acid titanium, is mixed with the start raw material of CaHAP, i.e., a calcium nitrate, by the specified quantity. The specified quantity in this case is Xmetal about it preferably. It is Xmetal= when it carries out. It is the amount which is set to  $Ti/(Ti+calcium)=0.03-0.11$  (mole ratio). In addition, although this convention is shown about the case where the metal atom exchanged is Ti and the metal atom (equivalent to A of the apatite previously shown by the general formula) of an apatite is calcium, in operation of this invention, this convention is effective also in the combination of the metal of possible others. Moreover, as for the sum density of metals, such as Ti, and metals, such as calcium, it is desirable to adjust so that it may become 0.1 mols. Subsequently, phosphoric acid is added into the obtained mixture, aqueous ammonia is added further, and pH is adjusted. As for pH at this time, it is desirable that it is about 9. Then, the obtained suspension is preferably aged over 6 hours at 100 degrees C, and is filtered further. If pure water washes the precipitate carried out the \*\* exception and it dries further, Ti ion-exchange CaHAP made into the object can be obtained. This remains as it is, may be used, or after applying to a suitable base material according to vacuum deposition, such as the applying methods, such as a spin coat, and sputtering, and the other technique and making with the gestalt of a thin film, it may be used.

[0020] The metal qualification apatite by this invention is useful in especially the field of electronics, can specifically be used in the display device installed in a restaurant, a public facility, etc., for example, PDP etc., and can be made maintenance free according to the self-cleaning effectiveness. Moreover, it can be used for the peripheral device of a computer, for example, a keyboard, a mouse, a case, etc., and adhesion of dirt, such as finger marks, can be prevented. Furthermore, it can be used for the optics (a mirror, lens, etc.) currently used in the interior, such as a touch panel and a printer, and the quantity of light attenuation which results from the dirt adhering to an optic can be controlled.

[0021]

[Example] Hereafter, it explains with reference to the example of this invention. In addition, please understand that this invention is not what is limited to the following example.

The pure water which carried out decarbonation processing of 1l. of preparation of example 1 Ti ion-exchange CaHAP (L) was prepared, and the sulfuric-acid titanium solution of a different amount from a 0.1-mol calcium nitrate was mixed and stirred to the pure water under nitrogen-gas-atmosphere mind.

The addition of the sulfuric-acid titanium in this case is  $X_{\text{metal}} =$  in order to investigate the effect of the amount of Ti in the composite material obtained. It changed so that  $\text{Ti}/(\text{Ti}+\text{calcium})$  might be set to 0, 0.01, 0.03, 0.1, and 0.5 and 0.8 (mole ratio). Moreover, Ti and calcium sum density were 0.1 mols. Subsequently, 0.06-mol phosphoric acid was added into the obtained mixture, the aqueous ammonia of 15 more mols / L was added, and pH was adjusted so that it might be set to 9.00. Then, the obtained suspension was moved to the Teflon TM bottle, and it aged over 6 hours at 100 degrees C. The suspension which precipitate generated was filtered, and the pure water of 5L washed the precipitate which classified, and it dried over 12 hours in 70 more-degree C dry oven. CaHAP (it is hereafter described also as CaHAP) without Ti ion exchange and CaHAP (it is hereafter described also as Ti-CaHAP) by which Ti ion exchange was carried out were obtained.

CaHAP and Ti-CaHAP which were prepared in the characterization aforementioned example 1 of example 2 CaHAP and Ti-CaHAP were used as a sample, and characterization was performed about each item of TEM, XRD, XPS, and FT-IR. Below, the result is explained.

(1) The gestalt of the sample of each observation of a crystalline form was observed using the transmission electron microscope (TEM) made from JEOL. Ti addition, i.e.,  $X_{\text{metal}}$ , It was checked that the gestalt is changing from the ellipse form to the shape of a needle it having been checked that the sample to 0.1 consists of a uniform particle, and the crystal structure of HAP being held with the increment in Ti addition. Furthermore,  $X_{\text{metal}}$  When 0.1 was exceeded, it became clear that the infinite form particle considered to be the cylindrical giant particle and phosphoric acid titanium hydrate of HAP generates, respectively.

(2) XRD (X diffraction) estimated the crystallinity of the sample of each crystalline assessment more. Consequently, as shown in the graph of drawing 4, it was checked that crystallinity is falling with the increment in Ti addition.

(3) Although many Ti ion to the interior of a particle existed from the surface analysis (the photoelectron spectroscopy equipment by PerkinElmer, Inc. is used) by XPS of the sample of each surface analysis, and the surface analysis (the FT-IR equipment by PerkinElmer, Inc. is used) by FT-IR, in  $X_{\text{metal}}=0.1$ , it became clear to exist as Ti-OH in the front face of some particles. Drawing 5 is the graph which showed FT-IR spectrum of each sample.

[0022] In the sample from the above assessment results to about  $X_{\text{metal}}=0.1$ , it became clear for the ion exchange of Ti to the inside of HAP to be effectively possible. Moreover, it is clear that this conclusion's [ especially ] it can apply similarly to other metal qualification apatites contained in the range of this invention not to mention Ti-CaHAP checked by this example.

Pressing of CaHAP ( $X_{\text{metal}}=0$ ) and Ti-CaHAP ( $X_{\text{metal}}=0.1$ ) which were prepared in the assessment aforementioned example 1 of example 3 photocatalyst activity was carried out to the tablet which has the respectively same specific surface area, and it was used as a sample. The seal desiccator permuted with synthetic air is prepared, and gaseous-phase concentration is 200 ppm about a sample and an acetaldehyde ( $\text{CH}_3\text{CHO}$ ) steam. It introduced until it became. Subsequently, ultraviolet-rays light with a quantity of light of 2.12mW was irradiated over 24 hours from the upper part of a desiccator, after that, spacing of 24 hours was opened and the ultraviolet-rays light of the same quantity of light was irradiated over 24 hours. A result which is plotted to drawing 7 about the sample which it becomes from Ti-CaHAP ( $X_{\text{metal}}=0.1$ ) as a result of plotting to drawing 6 about the sample which consists of CaHAP ( $X_{\text{metal}}=0$ ), when the concentration of the carbon dioxide gas ( $\text{CO}_2$ ) which occurred by the acetaldehyde gas in a desiccator and its decomposition is measured by the gas chromatography was obtained, respectively. In addition, in each drawing, Curve I and Curve II show the concentration of acetaldehyde gas and carbon dioxide gas, respectively, and ON and OFF show the timing of the exposure of ultraviolet-rays light, and an exposure halt, respectively.

[0023] In the case of the sample which consists of CaHAP ( $X_{\text{metal}}=0$ ) which is an example of a comparison, the increment in the concentration of the carbon dioxide gas by the exposure of ultraviolet-rays light was hardly able to be accepted so that I might be understood from the result plotted to drawing 6 and drawing 7. In addition, although there was an increment in some [ of the concentration of carbon dioxide gas ] by the exposure of the 1st ultraviolet-rays light, since it is changeless, this is understood to

be a thing originating in the carbon dioxide gas with which it adsorbed from the beginning into the sample also by the exposure of the 2nd ultraviolet-rays light. On the other hand, in the case of the sample which consists of Ti-CaHAP ( $X_{\text{metal}}=0.1$ ) which is an example of this invention, there is a remarkable increment in the concentration of carbon dioxide gas at each time of an exposure of ultraviolet-rays light, and it became clear to have the outstanding photocatalyst activity.

[0024]

[Effect of the Invention] As explained above, according to this invention, the apatite which can maintain the outstanding specific adsorption property over specific sorbates, such as the organic substance, which the catalyst function in which various kinds of apatites including calcium hydroxyapatite do so is developed further, and can be made to discover a new photocatalyst function and originates in an apatite simultaneously over a long period of time and by which metal qualification was carried out can be offered. Moreover, according to this invention, the approach that the outstanding apatite by this invention by which metal qualification was carried out can be manufactured with simple and high dependability can also be offered.

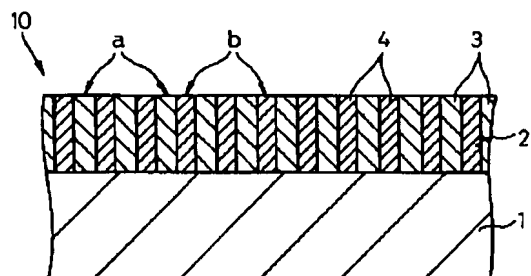
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Drawing selection drawing 1 ☒

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